TITLE: **Study of Solvent and Catalyst Interactions in Direct Coal Liquefaction**

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ABSTRACT

The role of the catalyst and the solvent in direct coal liquefaction is not very well understood. There have been many attempts to produce ultrafine catalysts in the expectation that better contact between catalyst and coal might result. This approach had only limited success probably because mass transfer between two solids in a fluid medium i.e. the catalyst and the coal, is very poor. This project aimed at understanding the interaction between the solid catalyst, the coal and the solvent in direct liquefaction reactions. One objective of this project is to determine whether intimate contact between catalyst and coal is necessary in liquefaction processes. If this is not the case, then what is the actual process of communication within the solvent between the catalyst and the coal.

The second part of this project was concerned with the different performance of different coal rank in liquefaction reactions. It is known that certain ranks of coal are more amenable to liquefaction (i.e. have higher liquefaction yields) than others. Volatile matter is one of the parameters that varies with coal rank but little is known about the chemical identity of the volatile matter. A technique for characterizing the volatile matter was developed and the various volatile products were described as a function of coal rank.

Thus the specific objectives were: 1) to test necessity of direct contact between catalyst and coal during coal liquefaction, 2) to investigate the role of the solvent as a transfer medium between the catalyst and the coal particles, 3) and to examine the chemical composition of different rank coals and use it as a guideline for "good" liquefaction coals.

RESULTS

To determine whether close contact between catalyst and coal is necessary, a series of liquefaction experiments were made using a short contact time batch reactor with the solid catalyst in a stainless steel basket placed in the reactor. Several baskets of different porosity were used; 450 µm, 0.5µm, 2µm, and 5µm. The basket insured that there was no direct contact between the coal and the catalyst. We also ran experiments with an empty basket (non-catalytic) in order to compare the coal conversion between a catalytic and non-catalytic reactions.

The liquefaction was carried out with 1 : 8 coal to solvent ratio. To better understand the role of the solvent in the presence and absence of a solid catalyst, a series of liquefaction experiments were conducted using solvents with various hydrogen donor ability. In addition to tetralin which is known as a strong hydrogen donor, decalin and methylnaphthalene were used. Decalin was an example of a poor hydrogen donor while methylnaphthalene is considered intermediate hydrogen donor. The activity of a separated catalyst (in the basket) was observable in the case of decalin while it was not clearly visible in the case of methylnaphthalene. While these results need further clarification one implication may be that the coal conversions in catalytic reactions are less sensitive to the hydrogen donor capacity of the solvent then to the presence of gaseous hydrogen. A further confirmation of this was provided by reactions where part of the tetralin solvent was replaced with very strong donors such as 1,2-dihydronaphthalene and 9,10-dihydrophenanthrene. The coal conversions did not increase appreciably when these stronger donors were added to tetralin.

Variation of volatile matter with coal rank was established using a thermogravimetric analyzer. The specific correlation that was established on more then 28 coals was the variation of the peak temperature of volatile matter evolution with coal rank. A smaller subgroup of these coals were analyzed by thermogravimetry -photoionization mass spectrometry (TG-PI-MS) which enabled the characterization of classes of compounds that are part of the volatile matter. Several trends with coal rank were observed. First, the relative amounts of oxygen-containing compounds such as $C_nH_{2n}O$, phenols, and dihydroxybenzenes decrease with increasing coal rank. Second, the relative amounts of aromatic hydrocarbons such as naphthalenes, phenanthrenes, and pyrenes increase with increasing coal rank. The higher stability of aromatic relative to aliphatic compounds may contribute to the increase in the temperature of maximum volatile matter evolution with increasing coal rank.

Two separate techniques confirmed that the majority of compounds detected by TG-PI-MS were products of thermal bond cleavages and not thermal desorption. Part of the volatile matter detected by TG-PI-MS may be removed by solvent extraction with either THF or pyridine. The relative intensities of compounds evolved from the solvent extract, the coal after extraction, and the raw coal remain virtually identical. This suggests that the volatile matter consists of a range of molecular weights with similar molecular structures.

ARTICLES AND STUDENT SUPPORT

1. "Thermogravimetric and Rock-Eval Studies of Coal Properties and Coal Rank," H. Huang, S. Wang, K. Wang, M.T. Klein, W.H. Calkins and A. Davis *Energy Fuels*, **13**, 396-400, 1999.

2. "Thermogravimetry-Photoionization Mass Spectrometry of Different Rank Coals," D.L. Zoller, M.V. Johnston, J. Tomic, X.Wang and W.H. Calkins *Energy Fuels*, **13**, 1097-1104, 1999.

3. "Interaction of Solid Catalyst and Solvents in Direct Coal Liquefaction," J. Tomic, X.Wang and W.H. Calkins, to be submitted for publications.

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